#### INFORMATION ONLY QA: QA



# USE OF TITRATION CALORIMETRY TO DETERMINE REACTION HEAT

Technical Implementing Procedure ID: OSTI-LBNL-TIP/GCT-3.0, Rev.0, Mod.0

Effective: 09/17/04

#### 1. PURPOSE

This Technical Implementation Procedure (TIP) describes the process used to determine reaction heat by titration calorimetry at Lawrence Berkeley National Laboratory (LBNL) for supporting the Office of Science & Technology and International (OSTI)-LBNL Project. This research is a part of the project entitled "Actinide Thermodynamics at Elevated Temperatures". The significance of this research is described in OCRWM-OSTI-TP-DC Rev.1, *Test Plan for Actinide Thermodynamics at Elevated Temperatures*, Section I: Introduction.

The heat of complexation between actinide/lanthanide ions and selected ligands, including fluoride and sulfate, in aqueous solutions will be determined. From the reaction heat, the enthalpy of complexation will be calculated. These data, in conjunction with the stability constants, will be used to predict the effect of temperature on the complexation.

## 2. SCOPE

This procedure applies to the use of titration calorimetry to determine reaction heat to be performed by all OSTI-LBNL personnel for OSTI-LBNL activities subject to the U.S. Department of Energy (DOE) Office of Civilian Radioactive Waste Management (OCRWM) *Quality Assurance Requirements and Description* (QARD), DOE/RW-0333P. Prior to conducting work described in Section 3 of this procedure, personnel performing calorimetry require training in accordance with OSTI-LBNL Quality Implementing Procedure (QIP)-2.0, *Indoctrination and Training of Personnel*.

If this procedure cannot be implemented as written, OSTI-LBNL personnel shall notify the responsible Principal Investigator (PI). If it is determined that a portion of the work cannot be accomplished as described in this TIP, or would produce undesirable results, that portion of the work shall be stopped and not resumed until this procedure is modified per OSTI-LBNL-QIP-5.0, *Preparing the Quality Assurance Plan and Quality/Technical Implementing Procedures*.

If the responsible PI determines that a modification or a revision to the TIP would cause an unreasonable delay in proceeding with the task, then an expedited change to the procedure, including documentation of deviation from the approved procedure, can be made according to OSTI-LBNL-QIP-5.0. Such changes are subject to review, usually after the task has proceeded, and thus work performed under TIPs with expedited changes is done at risk of future invalidation.

Scientific staff may use copies of this procedure printed from the information only electronic file; however, scientific staff are responsible for assuring that the correct revision of this procedure is used. When this procedure becomes obsolete or superseded, it must be destroyed or marked

"superseded" in accordance with OSTI-LBNL-QIP-6.0, *Controlled Documents*, to ensure that this document is not used to perform work.

#### 3. PROCEDURE

#### 3.1 Principle

Titration calorimeters are used to measure the heats released (or absorbed) when a solution in the titration vessel is titrated with a titrant, and determine the enthalpy of reaction. For a titration of complexation reaction, the net experimental heat of reaction at the *i*th addition,  $Q_{i,r}(\exp)$ , is obtained by

$$Q_{i,r}(\exp) = Q_i - Q_{i,d} \tag{1}$$

where  $Q_i$  and  $Q_{i,d}$  are the total heat and the heat of "dilution" at the *i*th addition, respectively.  $Q_{i,d}$  is determined in a separate dilution experiment. Theoretically, the heat of reaction can be calculated by

$$Q_{i,r}(cal) = \Sigma(\Delta H_p \times \Delta n_p)$$
 (2)

where  $\Delta H_{\rm p}$  is the enthalpy of complexation of species "p" while  $\Delta n_{\rm p}$  is the change of moles of species "p" at the *i*th addition.  $\Delta n_{\rm p}$  is obtained by speciation calculations with known stability constants of the complexes. Calculation of  $\Delta H_{\rm p}$  is accomplished with a minimization program, Letagrop, to compare and minimize the difference between  $Q_{\rm i,r}({\rm cal})$  and  $Q_{\rm i,r}({\rm exp})$ .

# 3.2 Equipment

The equipment associated with this TIP consists of:

- A. A microcalorimeter (ITC-4200).
- B. A solution calorimeter (ISC-4300).

#### 3.3 Calibration Procedure

- A. Electrical calibration: The calorimeters are calibrated electrically by putting a precisely defined current through an electrical resistance heater for a precise amount of time, so that the exact heat released to the titration assembly can be accurately calculated. A calibration factor (for the ITC-4200) or the heat capacity of the titration assembly (for the ISC-4300) is calculated from the calibration, and used in the calculation of reaction heat in the titration.
- B. Chemical calibration: A chemical calibration utilizes a chemical reaction with known enthalpy to test all aspects of the instrument and the associated programs controlling the titration and calculating the enthalpy. A solution of American Chemical Society (ACS) reagent grade tris(hydroxymethyl) aminomethane (THAM) (0.9 mL and 0.1 mol.dm<sup>-3</sup> for the ITC-4200, 20.0 mL and 0.5 mol.dm<sup>-3</sup> for the ISC-4300) is titrated

with standardized HCl ( $5.00-10.0~\text{mmol.dm}^{-3}$  for the ITC-4200 and  $1.0~\text{mol.dm}^{-3}$  for the ISC-4300) and the enthalpy of protonation of THAM is calculated. The expected  $\Delta H(\text{protonation})$  is  $-(47.5\pm1.0)~\text{kJ mol}^{-1}$  at 25 °C. Since the result of the chemical calibration depends on the calibration factor obtained by the electrical calibration, an electrical calibration always needs to be performed prior to a chemical calibration.

Both electrical and chemical calibrations need to be performed before the calorimetric study of the complexation systems. Document each calibration of the calorimeters in the scientific notebook using the M&TE Calibration Documentation form or equivalent per OSTI-LBNL-QIP-12.0, *Control of Measuring and Test Equipment and Calibration Standards*.

# 3.4 Data Acquisition and Reduction

Both calorimeters are controlled by computers and data acquisition is started by interactively following the instructions on the display and the instrument manual (CSC 4200, User's Manual, Section 6: Operation). General procedures for the titration of reaction (to obtain  $Q_i$  in Equation 1) and the dilution (to obtain  $Q_{i,d}$  in Equation 1) are described as follows:

- 3.4.1 Titration of reaction: 1) Place 0.90 mL titrate solution in the titration cell, attach the cell to the titration assembly and tighten it be hand, and insert the titration assembly into the calorimeter. 2) In parallel, place 0.90 mL water in the reference cell and insert the reference assembly into the calorimeter. 3) Fill 0.25 mL titrant in the 0.25 mL syringe and insert the syringe needle into the titration assembly. 4) When the baseline becomes stable (the baseline reading at 25 °C should be less than 15 microwatts), start the titration. The volume of titrant added at each step is usually set at 2 5 microliters. The total heat including those from the reaction and the dilution,  $Q_i$ , is obtained from this titration.
- 3.4.2 Dilution: The procedures for the dilution are exactly the same as those for the titration of reaction in Section 3.4.1, except that 0.90 mL blank solution (with the background electrolyte but without the particular reagent to react with the titrant), instead of the titrate, is placed in the titration cell. The dilution heat,  $Q_{i,d}$ , is obtained from this dilution.
- 3.4.3 The net reaction heat,  $Q_{i,r}(\exp)$ , is the difference between  $Q_i$  and  $Q_{i,d}$  (Equation 1).

The concentrations of the components in the titrate and the titrant vary depending on the particular metal-ligand systems under study. These are recorded in the scientific notebooks according to OSTI-LBNL-QIP-SIII.0, *Scientific Notebooks*. Specific entries for each experiment include the following: the titrate volume, the component names and concentrations in the titrate, the component names and concentrations in the titrant. These parameters and the  $Q_{i,r}(\exp)$  are used in the calculation of the enthalpy of reaction with the minimization program Letagrop which will be qualified in accordance with OSTI-LBNL-QIP-SI.0, *Software Management*.

The printouts of raw data and computer calculations are filed chronologically in a designated Scientific Notebook Supplement (e.g., a ring binder) that displays a scientific notebook identifier of the notebook with which the supplement is associated, according to OSTI-LBNL-QIP-SIII.0.

Document each use of the calorimeters on the M&TE Standard Usage Log from OSTI-LBNL-QIP-12.0, which is filed in the Equipment Logbook, with cross-reference to the scientific notebook.

#### 3.5 Potential Sources of Error and Uncertainty

Potential sources of error and uncertainty may result from human error in the preparation of solutions and/or from severe fluctuations of ambient temperature in the calorimeter lab. Multiple titrations are performed with individual complexation systems to identify the error and reduce the uncertainty.

#### 3.6 Controls for Out-of-Calibration Conditions

If any out-of calibration conditions (as described in OSTI-LBNL-QIP-12.0) are determined to exist for a M&TE item (e.g., instrument produces results known to be in error), the instrument shall have an out-of-service tag applied indicating that it is not to be used, and when possible, the instrument shall be moved to a segregated "out-of-service" area.

The above conditions shall be documented by using the M&TE Out of Calibration Report (OCR) in accordance with the instructions provided in OSTI-LBNL-QIP-12.0. If it is determined that the data are impacted, a Nonconformance Report (NCR) shall be initiated in accordance with OSTI-LBNL-QIP-15.0, *Nonconformances*.

#### 4. RECORDS

The records listed below shall be collected and submitted to the Records Coordinator for submittal to OSTI who in turn will submit records to the Records Processing Center (RPC) in accordance with OSTI-LBNL-QIP-17.0, *Records Management*, as individual records or included in a records package.

## 4.1 Quality Assurance (QA) Records

Records generated as a result of this TIP are entries in:

- Scientific notebooks or Supplements to such notebooks,
- Equipment Logbooks (including M&TE Justification Form, if appropriate, and Standard Usage Log)

# 4.2 Non-QA Long Term Records

None

#### **4.3** Non-QA Short-Term Records (three years or less retention)

None

#### 5. RESPONSIBILITIES

- **5.1** The **Principal Investigator (PI)** is responsible for assuring full compliance with this procedure and providing training thereof. The PI is responsible for overseeing and coordinating the preparation, review, distribution, revision, and recommending rescission of this TIP.
- **5.2 Scientific staff** are responsible for following this procedure and turning over related documentation to the Records Coordinator for submittal to the OSTI in accordance with OSTI-LBNL-QIP-17.0. Related data shall be turned over to Technical Data Coordinator in accordance with OSTI-LBNL-QIP-SIII.3, *Submittal and Incorporation of Data to the Technical Data Management System*, for entry into the Technical Database Management System (TDMS).

#### 6. ACRONYMS AND DEFINITIONS

## 6.1 Acronyms

ACS American Chemical Society

DOE Department of Energy

GCT Geochemical Testing

LBNL Lawrence Berkeley National Laboratory

M&TE Measuring and Test Equipment

NCR Nonconformance Report

OCR Out of Calibration Report

OSTI Office of Science & Technology and International

PI Principal Investigator

QA Quality Assurance

QARD Quality Assurance Requirements and Description

QIP Quality Implementing Procedure

RPC Records Processing Center

TDMS Technical Data Management System

TIP Technical Implementing Procedure

THAM tris (hydroxymethyl) aminomethane

#### **6.2** Definitions

**Calorimeter:** An instrument that is capable of measuring the heat released or absorbed in a reaction vessel.

**Technical Implementing Procedure:** Each TIP describes YMP-LBNL technical tasks that (1) are repetitive, and (2) are standardized, and (3) can return different results if deviation from the sequence of steps occur.

#### 7. REFERENCES

DOE/RW-0333P, Quality Assurance Requirements and Description

OSTI-LBNL-QIP-2.0, Indoctrination and Training of Personnel

OSTI-LBNL-QIP-5.0, Preparing the Quality Assurance Plan and Quality/Technical Implementing Procedures

OSTI-LBNL-QIP-6.0, Controlled Documents

OSTI-LBNL-QIP-12.0, Control of Measuring and Test Equipment and Calibration Standards

OSTI-LBNL-QIP-15.0, *Nonconformances* 

OSTI-LBNL-QIP-17.0, Records Management

OSTI-LBNL-QIP-SIII.0, Scientific Notebooks

OSTI-LBNL-QIP-SIII.3, Submittal and Incorporation of Data to the Technical Data Management System

#### 8. ATTACHMENTS

None

# 9. REVISION HISTORY

09/17/04 Revision 0, Modification 0:

Initial issue.

# 10. APPROVAL

(Signature on File)	
Preparer/PI: Linfeng Rao	Date
(Signature on File)	-
Technical Reviewer: Katharine Woods	Date
(Signature on File)	
Technical Reviewer: Christopher Guay	Date
(Signature on File)	
QA Reviewer: Nancy Aden-Gleason	Date
(Signature on File)	
Project Manager: Gudmundur S. Bodvarsson	Date